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Experimental and numerical analysis of magnetic susceptibility of the tetranuclear heterometallic SMM complexes $[\text{Me}_2^{\text{II}}\text{Fe}_2^{\text{III}}(\text{L})_4(\text{OH})_2\cdot\text{EtOH})_2\cdot(\text{Et}_2\text{O})_2]$, Me = Co, Ni with dicubane structure

To cite this article: D Starichenko *et al* 2019 *J. Phys.: Conf. Ser.* **1389** 012020

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Experimental and numerical analysis of magnetic susceptibility of the tetranuclear heterometallic SMM complexes $[\text{Me}_2^{\text{II}}\text{Fe}_2^{\text{III}}(\text{L})_4(\text{OH})_2\cdot(\text{EtOH})_2\cdot(\text{Et}_2\text{O})_2]$, Me = Co, Ni with dicubane structure

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Abstract. Magnetic susceptibilities of the two isostructural heterometallic complexes, $[\text{Me}_2^{\text{II}}\text{Fe}_2^{\text{III}}(\text{L})_4(\text{OH})_2\cdot(\text{EtOH})_2\cdot(\text{Et}_2\text{O})_2]$, Me = Co, Ni, with triketonate ligands L = dianion of 1,1,1,7,7,7-hexa-fluoroheptane-2,4,6-trione, were studied experimentally and theoretically. Extended theoretical analysis included a phenomenological approach as well as quantum calculations in several numerical schemes. Magnetic ground states of $\text{Co}_2^{\text{II}}\text{Fe}_2^{\text{III}}(\text{L})_4$ and $\text{Ni}_2^{\text{II}}\text{Fe}_2^{\text{III}}(\text{L})_4$ complexes were resolved as an interplay of two intrinsic superexchange interactions with the constants J^{FeFe} and $J^{\text{CoFe}}/J^{\text{NiFe}}$. The first system was described by two non interacting AFM-coupled pairs Co-Fe with $J^{\text{CoFe}} = -4.2 \text{ cm}^{-1}$ and zero-field splitting parameter $D = -0.15 \text{ cm}^{-1}$. The second one revealed the ferromagnetic coupling between the AFM dimers, $J^{\text{NiFe}} = -12.1 \text{ cm}^{-1}$, $J^{\text{FeFe}} = 1.3 \text{ cm}^{-1}$ and $D = -0.5 \text{ cm}^{-1}$.

1. Introduction

A significant progress in design and synthesis of Single-Molecule ferro- and ferri- Magnets (SMMs) was achieved in a broad family of coordination metal-complexes with superexchange couplings in the intrinsic metal-oxygen cores [1]. Most of these SMM complexes had dicubane or polycubane architectures of the core. The most extensively studied system is a ferrimagnetic heterovalent $\text{Mn}_4(\text{hmp})_6$ family [2-4]. A character of the superexchange interactions among Mn^{3+} , $S = 2$, and Mn^{2+} , $S = 5/2$, is determined by the occupied $3p$ -orbitals of the hydroxy group of the (hmp) ligand [5]. Two of other three sp^2 orbitals form chemical bonds, and all three of them do not take part in the superexchange. The specific non-hybridized $3p$ -orbital, which mediated superexchange, is orthogonal to the COH plane for each (hmp) ligand. Its orientation regarding to the chelate plane affects both magnitude and sign in each Me-Me' of ten superexchange channels. Thus an individual tetranuclear $\text{Mn}_4(\text{hmp})_6$ complex has an entangled character of interconnected pair exchange couplings between metal ions, which depend on the chemical variations of the ligand. The published theoretical calculations still have opaque sides in explaining the linkage between the structure peculiarities and the ground spin state [6]. Existing numerical approaches for quantum calculations via diagonalization of the Heisenberg-Van Vleck Hamiltonian were limited by multiplicity $4 \times 5/2$. These schemes cannot be



applied to the novel polynuclear SMMs and coordination complexes of rare-earth metals. Therefore new numerical approaches are required. In this work we applied the advanced full-diagonalization numerical scheme realized in ALPS (Algorithms and Libraries for Physics Simulations). Two isostructural dicubane molecules revealing different ground spin states were analyzed. Experimental temperature dependence of their spin susceptibilities were calculated and compared by using three approaches: semi-empirical (hierarchical Bleaney-Bowers dimers), approximate fitting method (julX, Heisenberg-Van Vleck model), extended full-diagonalization approach (ALPS, Heisenberg-Van Vleck model). Satisfactory agreement with the experiment was achieved for all three methods. Thus the ground spin state of both molecules was resolved and explained. The ALPS method is now available for calculations of polynuclear SMM systems including rare-earth complexes.

2. Experimental

2.1. Synthesis and structure

A family of tetranuclear triketonates is extended by a series of the heterometallic complexes $[\text{Me}_2^{\text{II}}\text{Fe}_2^{\text{III}}(\text{L})_4(\text{OH})_2\cdot(\text{EtOH})_2\cdot(\text{Et}_2\text{O})_2]$, $\text{Me} = \text{Co}$ (**1**), Ni (**2**), L =dianion of 1,1,1,7,7,7-hexafluoroheptane-2,4,6-trione, obtained by means of reaction of $[\text{Me}_2^{\text{II}}(\text{L})_2\cdot 4\text{H}_2\text{O}]$ with $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ [7,8]. Distorted dicubane geometry was determined for the metal-oxygen $\text{Me}_2^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_6$ core by the single-crystal X - ray analysis of polycrystal samples (figure 1a). All metal ions were 6-coordinated in elongated octahedral environment, which was formed by a combination of μ_2 -triketonato and μ_3 -hydroxo oxygen atoms. By arrangement the core resembles a family of the heterovalent complexes of $\text{Mn}_4(\text{hmp})_6$ showing ferromagnetic SMM properties [9].

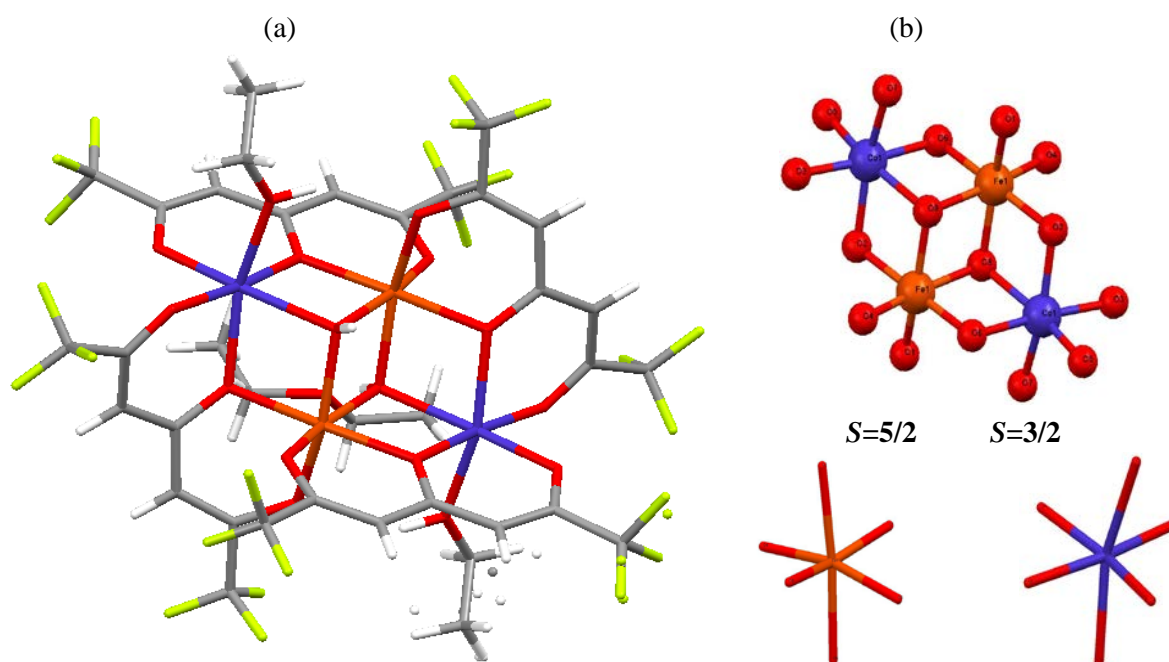


Figure 1. (a) The structure of the complex $\text{Co}_2\text{Fe}_2(\text{L})_4$ (**1**) from X-ray analysis. (b) Metal-oxygen core. The octahedral environment of Co^{2+} ($S = 3/2$) and Fe^{3+} ($S = 5/2$) ions.

2.2. SQUID magnetometry

Magnetic data for the complexes **1**, **2** were collected on a Quantum Design MPMS-5L SQUID magnetometer. Measurements were performed on microcrystalline samples in a polyethylene bag. Prior to magnetic measurements, all samples have been characterized by a powder X - ray diffraction for comparison with the reference single crystal data. The magnetic data were corrected by taking into account the diamagnetic contributions from the molecular structure and the sample holder.

Static magnetic susceptibility, $\chi(T)$, was measured in the interval 2.0 to 300 K in the external field 1 and 40 kG. Contribution of ferromagnetic impurities was found negligible.

X-band CW EPR measurements were also done and did not reveal EPR signals.

3. Results and discussion

3.1. Structure and semi-empirical analysis of magnetic properties

The bond lengths (table 1) and internal angles (table 2) of the metal-oxygen core were determined by the analysis of the structural CIF files (crystal information file) (figure 1b). The metal-oxygen core was found symmetric.

Table 1. Metal-oxygen bond lengths for **1**.

Bond	Length, Å	Bond	Length, Å
Co ⁽¹⁾ -O ₂ ⁽¹⁾	2.099	Co ⁽²⁾ -O ₂ ⁽²⁾	2.099
Co ⁽¹⁾ -O ₃ ⁽¹⁾	2.024	Co ⁽²⁾ -O ₃ ⁽²⁾	2.024
Co ⁽¹⁾ -O ₅ ⁽¹⁾	2.011	Co ⁽²⁾ -O ₅ ⁽²⁾	2.011
Co ⁽¹⁾ -O ₆ ⁽¹⁾	2.110	Co ⁽²⁾ -O ₆ ⁽²⁾	2.110
Co ⁽¹⁾ -O ₇ ⁽¹⁾	2.054	Co ⁽²⁾ -O ₇ ⁽²⁾	2.054
Co ⁽¹⁾ -O ₈ ⁽¹⁾	2.135	Co ⁽²⁾ -O ₈ ⁽²⁾	2.135
Fe ⁽¹⁾ -O ₁ ⁽¹⁾	1.959	Fe ⁽²⁾ -O ₁ ⁽²⁾	1.959
Fe ⁽¹⁾ -O ₂ ⁽²⁾	2.015	Fe ⁽²⁾ -O ₂ ⁽¹⁾	2.015
Fe ⁽¹⁾ -O ₄ ⁽¹⁾	1.925	Fe ⁽²⁾ -O ₄ ⁽²⁾	1.925
Fe ⁽¹⁾ -O ₆ ⁽¹⁾	2.027	Fe ⁽²⁾ -O ₆ ⁽²⁾	2.027
Fe ⁽¹⁾ -O ₈ ⁽¹⁾	2.024	Fe ⁽²⁾ -O ₈ ⁽²⁾	2.024
Fe ⁽¹⁾ -O ₈ ⁽²⁾	2.033	Fe ⁽²⁾ -O ₈ ⁽¹⁾	2.033

Table 2. Internal angles of the metal-oxygen core for **1**.

Bond	Angle, °
Fe ⁽¹⁾ -O ₈ ⁽¹⁾ -Fe ⁽²⁾	101.15
Co ⁽¹⁾ -O ₆ ⁽¹⁾ -Fe ⁽¹⁾	101.26
Co ⁽¹⁾ -O ₈ ⁽¹⁾ -Fe ⁽²⁾	100.89
Co ⁽¹⁾ -O ₂ ⁽¹⁾ -Fe ⁽²⁾	102.77
Fe ⁽²⁾ -O ₈ ⁽²⁾ -Fe ⁽¹⁾	101.15
Co ⁽²⁾ -O ₆ ⁽²⁾ -Fe ⁽²⁾	101.26
Co ⁽²⁾ -O ₈ ⁽²⁾ -Fe ⁽²⁾	100.52
Co ⁽²⁾ -O ₈ ⁽²⁾ -Fe ⁽¹⁾	100.89
Co ⁽²⁾ -O ₂ ⁽²⁾ -Fe ⁽¹⁾	102.77

According to semi-empirical Goodenough-Kanamori rules, the sign of superexchange interaction in the neutral complex is determined by the symmetry of atomic and ligand orbitals and the angle between the coordinating oxygen *p*-orbital and the *d*-orbitals of the adjacent metal ions, Me-O-Me'. The sign changes when the angle exceeds a critical value. Since all Fe-O-Fe and Co-O-Fe angles are wider than the critical 99°, one can assume that all superexchange interactions Fe³⁺-Fe³⁺ and Co²⁺-Fe³⁺ ions are supposed to be antiferromagnetic. For Fe³⁺ and Co²⁺ ions in octahedral environment, the *t_{2g}-e_g* splitting take place. Respectively, *d_z²* and *d_{x²-y²}* orbitals take part in the exchange interactions.

The strength of the electrostatic ligand field is determined by strong CO groups of the triketonate. However, the terminal fluoromethyl groups have large electronegativity. They polarize the entire ligand and weaken the ligand field, affecting the spin-orbital splitting value, Δ . In addition, the distortions of the octahedral environment further reduce the Δ factor. Therefore, fluorinated triketone is a ligand of a less strong field, the splitting value Δ is less than that due to stronger intra-atomic Hund exchange the high spin configuration was realized. Therefore, the spin states of Fe³⁺ and Co²⁺ ions were 5/2 and 3/2, respectively (figure 1c).

The experimental values of the product $\chi T(300\text{ K})$ were 14.1 cm³ K/mol (**1**) and 9.4 cm³ K/mol (**2**) (figure 2). They are consistent with the theoretical values: 12.5 cm³ K/mol - for two paramagnetic Fe³⁺ ions with $S = 5/2$ and two Co²⁺ ions with $S = 3/2$ (**1**); and 10.7 cm³ K/mol - for two pairs of Ni²⁺, $S = 1$ and Fe³⁺, $S = 5/2$ (**2**). The deviations are caused by spin-orbit

contribution, Δg ($g_{\text{exp}} \neq g_{\text{theor}}=2$), and non-paramagnetic behavior χT in the vicinity of 300 K. At cooling down to 30 K χT gradually decreased indicating on antiferromagnetic (AFM) interactions in both systems. At lower temperatures the behavior was qualitatively different. For **1** it reached the minimum at $T = 2.0$ K, $\chi T = 1.5$ cm³ K/mol ($B = 0.1$ T). For **2** it reached maximum at $T = 3.2$ K, $\chi T = 5.4$ cm³ K/mol. This behavior is an indication of a ferrimagnetic spin alignment with incomplete compensation.

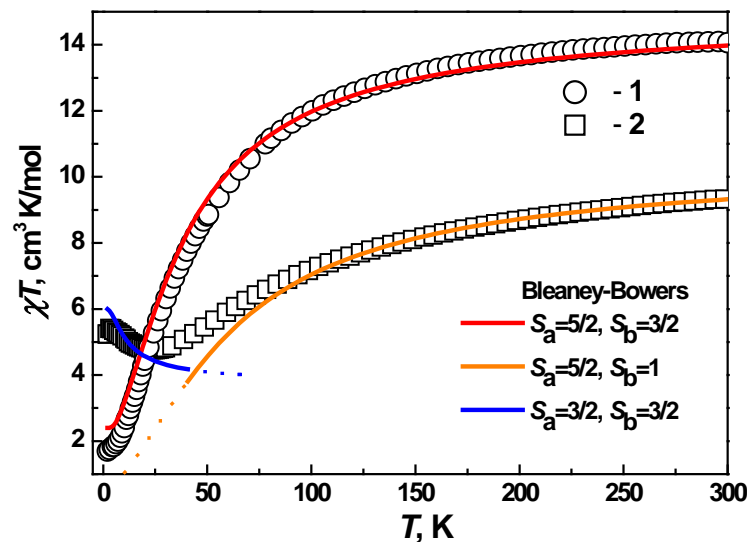


Figure 2. Experimental dependences of the product χT vs T for **1** (o) and **2** (□) and results of qualitative theoretical approach within Bleaney-Bowers model: solid red line – AFM Fe-Co dimers; solid orange line – AFM Fe-Ni dimers; blue line – FM coupled dimers. Numerical parameters are discussed in text.

The insets in figures 3, 4 show the temperature dependences of the reverse magnetic susceptibility, $\chi^{-1}(T)$. The Curie-Weiss approximation with the Curie constant $C = 15.3$ cm³ K/mol and the Weiss temperature $\Theta = -22.7$ K (**1**) fits well the data in the range 150 - 300 K. Similarly, the parameters $C = 11.0$ cm³ K/mol and $\Theta = -53.5$ K correspond to the best fit for **2**. The negative sign of Θ favor for AFM correlations.

The dicubane structure of the metal-oxygen core (figure 1b) and the specific angles (table 2) reveal two actual superexchange channels: Co-Fe/Ni-Fe and Fe-Fe. Contributions of Co-Co/Ni-Ni exchange interactions not-linked via the oxygen are insignificant. Taking into account a symmetry, we suggest a simple model with two exchange constants $J_1^{\text{CoFe/NiFe}}$ и J_2^{FeFe} . This model does not have an analytical expression for the general case. In the case, $|J_2| \sim 0$ it reduces to Bleaney-Bowers equation, describing the temperature dependence $\chi(T)$ of the dimeric phase [10]:

$$\chi = \frac{N_A g^2 \mu_B^2}{3kT} \frac{\sum_s S(S+1)(2S+1)e^{-E(J,S)/kT}}{\sum_s (2S+1)e^{-E(J,S)/kT}} \quad (1)$$

where $E(J,S) = -J[S(S+1) - S_a(S_a+1) - S_b(S_b+1)]$, $S = S_a + S_b, S_a + S_b - 1, \dots, |S_a - S_b|$ - total spin value. When $J_1 \gg J_2$ the qualitative approach allows considering the system as weakly coupled chain. Each dimer follows Bleaney-Bowers curve at $kT \gg J_2$, while it behaves as an effective magnetic moment in the homogeneous spin pair with J_1 at $kT \leq J_1$. This approach gives an opportunity of analytical description of heterometallic dicubane spin core.

In the case $S_a = 5/2$ and $S_b = 3/2$ (**1**) the Bleaney-Bowers equation reduces to the expression:

$$\chi = \alpha \frac{2N_A g^2 \mu_A^2}{3kT} \frac{180e^{15J/(2kT)} + 84e^{-J/(2kT)} + 30e^{-13J/(2kT)} + 6e^{-21J/(2kT)}}{9e^{15J/(2kT)} + 7e^{-J/(2kT)} + 5e^{-13J/(2kT)} + 3e^{-21J/(2kT)}} \quad (2)$$

Fitting to the experimental curve gives $\alpha = 1.2$, which takes into account a deviation of Fe and Co g -factors, and $J/k = J_1/k = -4.0 \text{ cm}^{-1}$ ($|J_2|/k \ll 2.0 \text{ cm}^{-1}$) shown in figure 2.

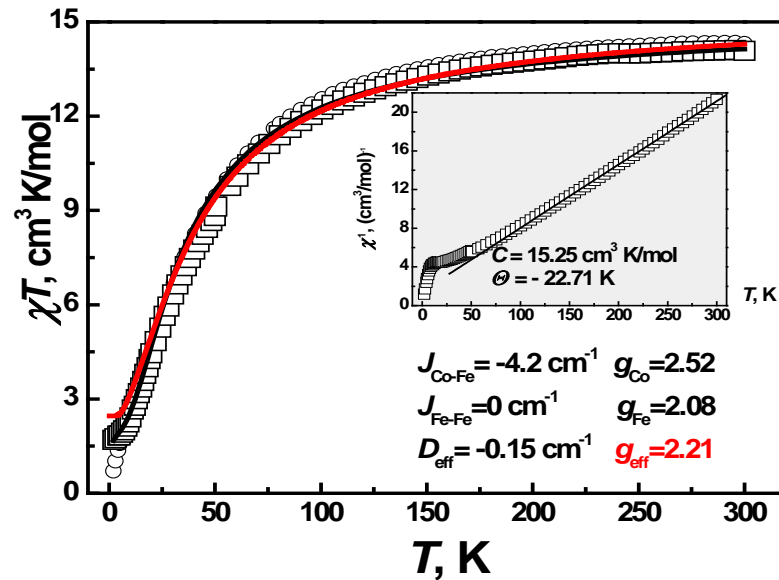


Figure 3. Temperature dependences of the product χT for **1**, measured at $B = 0.1$ (\square) and 4.0 T (\circ). Solid black line is theoretical julX fitting with the parameters J_1 , J_2 , g_1 , g_2 and D . Solid red line corresponds to ALPS calculations. The inset depicts reverse magnetic susceptibility $\chi^{-1}(T)$.

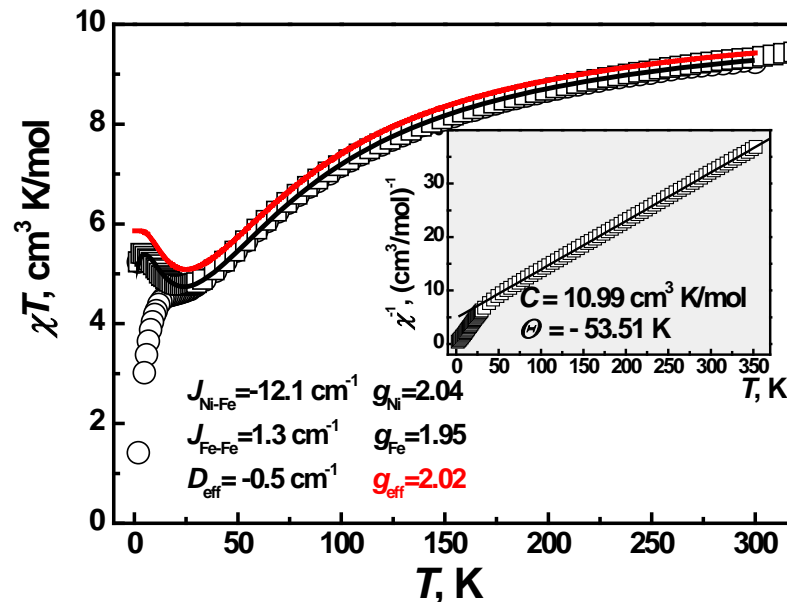


Figure 4. Temperature dependences of the product χT for **2**, measured at $B = 0.1$ (\square) and 4.0 T (\circ). Solid black line is theoretical julX fitting with the parameters J_1 , J_2 , g_1 , g_2 and D . Solid red line corresponds to ALPS calculations. The inset depicts reverse magnetic susceptibility $\chi^{-1}(T)$.

From this semi-empirical approach the ground spin state of the bimetallic tetranuclear dicubane **1** is antiferromagnetic with the estimates $J_1 = -4.0 \text{ cm}^{-1}$, $J_2 \approx 0$. At helium temperatures, $T < 6.0 \text{ K}$, the magnetic moments of Fe and Co ions of the core form two antiferromagnetically coupled pairs (dimers) with a total spin $S = S_{\text{Fe}} - S_{\text{Co}} = 1$. The respective theoretical estimate gives $\chi T = 2.0 \text{ cm}^3 \text{ K/mol}$ for $g = 2$. This is in reasonable agreement with the experimental value $1.5 \text{ cm}^3 \text{ K/mol}$ at $T = 2.0 \text{ K}$.

In the case $S_a = 5/2$ and $S_b = 1$ (**2**) the Bleaney-Bowers equation reduces to the expression:

$$\chi = \alpha \frac{2N_A g^2 \mu_B^2}{3kT} \frac{126e^{10J/(2kT)} + 52.5e^{-4J/(2kT)} + 15e^{-14J/(2kT)} + 1.5e^{-20J/(2kT)}}{8e^{10J/(2kT)} + 6e^{-4J/(2kT)} + 4e^{-14J/(2kT)} + 2e^{-20J/(2kT)}} \quad (3)$$

Fitting to the experimental curve gives $\alpha = 1.08$, which takes into account a deviation of Fe and Ni g -factors, and $J/k = J_1/k = -7.7 \text{ cm}^{-1}$ shown in figure 2. The equation (3) describes well the experimental data in the range $300 \div 100 \text{ K}$. In the intermediate range, $100 \div 24 \text{ K}$, an interplay of intrinsic of AFM and FM interactions determine the evolution of χT . Here we assumed that Fe-Fe FM coupling takes place between Ni-Fe dimers in **2**. For qualitative analysis we considered Fe-Ni dimer as an effective spin $S = S_{\text{Fe}} - S_{\text{Ni}} = 3/2$, interacting with the exchange constant J_2 . In fact, $S = 3/2$ spin is a Ni-Fe pair with AFM exchange constant J_1 . For two non-interacting $S = 3/2$ spins the theoretical estimate gives $\chi T = 3.75 \text{ cm}^3 \text{ K/mol}$. The experimental value $5.4 \text{ cm}^3 \text{ K/mol}$ is closer to the FM estimate of $6.0 \text{ cm}^3 \text{ K/mol}$. Therefore, we applied the Bleaney-Bowers equation for $S_a = 3/2$ and $S_b = 3/2$:

$$\chi = \alpha \frac{N_A g^2 \mu_B^2}{3kT} \frac{84e^{9J/(2kT)} + 30e^{-3J/(2kT)} + 6e^{-11J/(2kT)}}{7e^{9J/(2kT)} + 5e^{-3J/(2kT)} + 3e^{-11J/(2kT)} + e^{-15J/(2kT)}} \quad (4)$$

Satisfactory fitting was reached at $\alpha = 1.0$ and $J/k = J_2/k = 1.3 \text{ cm}^{-1}$ which is shown in figure 2.

3.2 Quantum calculations of the magnetic susceptibility

Quantum calculations were taken within the Heisenberg-Van Vleck model. First approach was performed by using the julX fitting program [11,12]. This numerical procedure includes full diagonalization of the following effective spin Hamiltonian:

$$H = H_z + H_{ex} + H_{ZFS} = g\mu_B \sum \vec{S}_i \cdot \vec{B} + \sum D_i (S_{z,i}^2 - 1/3 \cdot S_i(S_i + 1)) - 2J_{ij} \vec{S}_i \vec{S}_j \quad (5)$$

The Hamiltonian includes Zeeman (H_z) and exchange (H_{ex}) interactions and the rhombic part of the zero-field splitting tensor (H_{ZFS}). Non-axial ZFS constants were not taken into consideration. Magnetic moments were obtained from numerically generated derivatives of the eigenvalues of eq. 5, and summed up over 16 field orientations along a 16-point Lebedev grid to account for the powder distribution of the sample. Taking into account a symmetry of the complexes **1** and **2**, the number of independent fitting parameters for two $\text{Co}^{2+}/\text{Ni}^{2+}$ and two Fe^{3+} spin moments was reduced to five: the single ion g -factor $g_i = g_1, g_2$, where $g_1 = g_{\text{Co}}/g_{\text{Ni}}$, $g_2 = g_{\text{Fe}}$; the axial ZFS constant $D_i = D_1, D_2 = D_{\text{eff}}$ and the coupling constant $J_i = J_1, J_2$, where $J_1 = J^{\text{CoFe}}/J^{\text{NiFe}}$, $J_2 = J^{\text{FeFe}}$. Solid black lines in figures 3 and 4 depict the best-fit curves with the parameters presented in table 3.

Table 3. Numerical parameters of the theoretical calculations.

N_0	g_1/g_2	$\Theta, \text{ K}$	$C_{\text{exp}}, \text{ cm}^3 \text{ K/mol}$	$D_{\text{eff}}, \text{ cm}^{-1}$	$J_1/J_2, \text{ cm}^{-1}$
1	2.52/2.08	-22.7	15.25	-0.15	-4.2/0
2	2.04/1.95	-53.5	10.99	-0.5	-12.1/1.3

We also applied an alternative approach used the free ALPS library [13] as an alternative and more powerful software. In current realization, we did not consider different g -factors for individual atomic spin moments while calculating the static magnetic susceptibility, χ , leaving a single effective g -factor, g_{eff} . The values of g_{eff} were extracted from the experimental Curie constants, 2.21 and 2.02 for **1** and **2** complexes, respectively. This provided a good agreement of the calculated χT with the experimental data at high temperatures.

As for the exchange interactions, the results of julX calculations were used. The results of calculations are shown in figures 3 and 4 in the form of solid red lines.

4. Conclusions

Superexchange interactions and temperature evolution of the magnetic spin susceptibility were studied in the metal-oxygen cores of the isostructural coordination complexes $\text{Co}_2^{\text{II}}\text{Fe}_2^{\text{III}}(\text{L})_4$ (**1**) and $\text{Ni}_2^{\text{II}}\text{Fe}_2^{\text{III}}(\text{L})_4$ (**2**), where L is a fluorinated 1,3,5-triketone ligand. Molecular structure, experimental curves and semi-empirical analysis within the Bleaney-Bowers model gave rise to an assumption about two essential exchange couplings in the core: $J_1^{\text{CoFe}} = -4.0 \text{ cm}^{-1}$, $J_2^{\text{FeFe}} \ll 2.0 \text{ cm}^{-1}$ for **1** and $J_1^{\text{NiFe}} = -7.7 \text{ cm}^{-1}$, $J_2^{\text{FeFe}} = 1.3 \text{ cm}^{-1}$ for **2**. Quantum calculations in the Heisenberg-Van Vleck model with full diagonalization (julX) confirmed and improved phenomenological estimates: $J_1^{\text{CoFe}} = -4.2 \text{ cm}^{-1}$, $J_2^{\text{FeFe}} \ll 2.0 \text{ cm}^{-1}$, $g_1 = 2.52$, $g_2 = 2.08$, $D = -0.15 \text{ cm}^{-1}$ for **1** and $J_1^{\text{NiFe}} = -12.1 \text{ cm}^{-1}$, $J_2^{\text{FeFe}} = 1.3 \text{ cm}^{-1}$, $g_1 = 2.04$, $g_2 = 1.95$, $D = -0.5 \text{ cm}^{-1}$ for **2**. The alternative numerical approach, ALPS, was applied for validation of the quantitative data. All three theoretical approaches were consistent with experimental data. It is worth to note, that the ALPS method is not restricted by multiplicity and number of metal ions in comparison with julX. Thus ALPS becomes a prospective tool for microscopic analysis of the magnetic properties of polynuclear metal complexes including rare-earth metals.

Acknowledgments

The authors thank A.V. Korolev for magnetic measurements, V.Yu. Irkhin for discussion, and a synthetic team of the I. Ya. Postovsky Institute of Organic Synthesis (Russia, Ekaterinburg): D.L. Chizhov, P.A. Slepukhin, P.K. Novikova, D.C. Yachevskii, V.N. Charushin, for providing samples.

The research was carried out within the state assignment of Minobrnauki of Russia (theme "Spin" №AAAA-A18-118020290104-2 and "Structure" No. AAAA-A18-118020190116-6).

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